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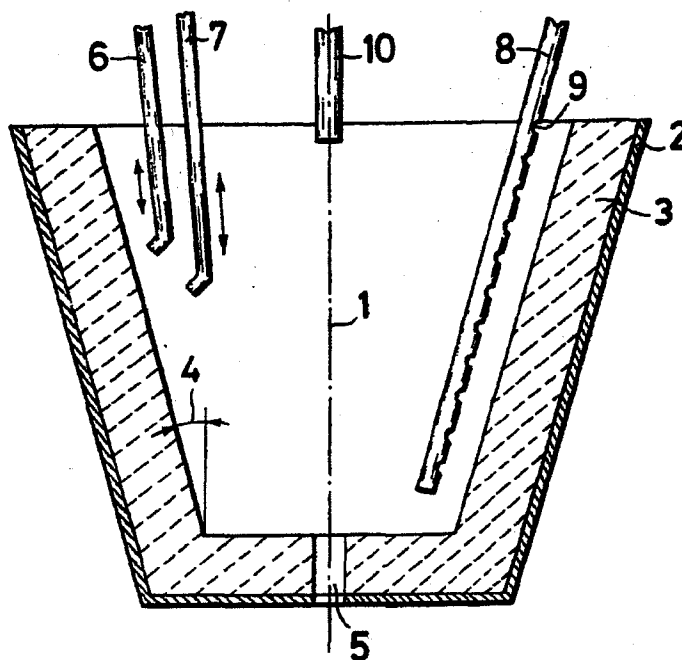
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(54) Recovering and concentrating non-ferrous materials such as zinc and lead

(57) A process for recovering or concentrating Zn and Pb from primary or secondary raw materials, admixed with coal, the coal being partially burnt to produce CO, is carried out in two stages, during the first of which there is direct

reduction of the material due to the effect of the coal and volatilization of zinc and of lead oxide, whereas in the second stage there is an oxidation in the vapour phase of the zinc produced in the first stage by the action of air and/or oxygen. An apparatus for carrying out the process is a reactor having a frustoconical outline and comprising a metal casing (2) internally lined with a refractory material (3) and rotated about its geometrically arranged vertical axis (1), the reactor being equipped with a bottom drain hole (5), for liquid material.

Fig.1



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Fig.1

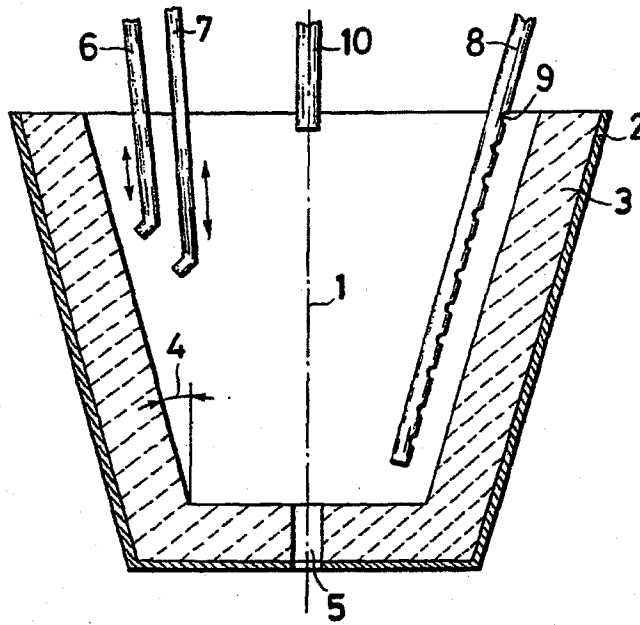
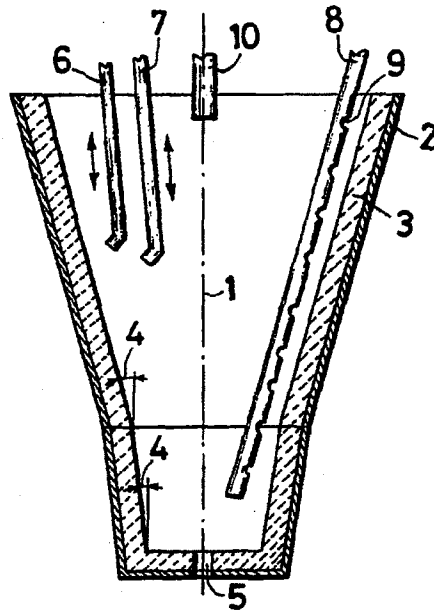


Fig.2



SPECIFICATION

Recovering and concentrating non-ferrous materials such as zinc and lead

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This invention relates to a process for enriching, with useful non-ferrous metals such as lead and/or zinc, by volatilization or fumigation at an appropriate temperature, materials which contain such metals in varying amounts in the form of oxides or sulphides of the metals. The materials used can either be primary raw materials (ores) or secondary raw materials (such as steel work fumes, mineral residues and metallurgical slags).

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The most important volatilization method used nowadays in order to recover or concentrate non-ferrous metals such as zinc and lead is the Waelz kiln method. In this method, the charge, which contains zinc (maximum 30% to 35%), lead, and other metals (to a lesser extent) is mixed with coke dust or anthracite dust in an amount of 18% to 25% by weight, and the mixture is charged into a conventional rotary kiln which is inclined by 2° to 4° relative to the horizontal.

Appreciable recovery of useful metals is thus obtained. The main shortcoming is the considerable bulk of the installation (due to the need to attain a very large exchange surface between the charge and atmospheric air) so that the sensible heat can be recovered only partially.

Another known process is the cyclone-oven process. In this process, the charge, mixed with coke dust, is put in a cylindrical cyclone oven wherein it is tangentially contacted by preheated air. The fumigation is completed in an adjacent oven which is generally an electric-arc furnace. In the electric arc furnace, non-volatile material can be collected in a blank phase which is separate from the slag. Thus, there is a considerable consumption of energy. Moreover, the charge must be completely dried and must have a particle size of one millimeter at the most.

It has now been surprisingly found that the drawbacks of the conventional methods can be overcome by using a single reaction zone having an environment which is partly oxidizing and partly reducing.

According to the present invention there is provided a process for treating a particulate material containing zinc in combined form, which comprises heating the material in the presence of a carbonaceous material so as to reduce the zinc in combined form to metallic zinc and so as to volatilize the metallic zinc, and effecting oxidation of the zinc in the vapour phase in the presence of air and/or oxygen.

In the process of the invention, poor-grade coal and small sized coal can be used instead of natural gas or coke. These advantages do not offset the possibility of obtaining a satis-

factory heat distribution pattern as well as the attainment of physico-chemical conditions which are suitable for the evolution of the reactions which are of interest.

In the process of the invention, there is used a mixture of a material which contains lead and zinc in the form of their oxides or salts (such as sulphates, sulphides, silicates, aluminates and others) and a carbon-containing material. During the process, partial combustion of the carbon produces carbon monoxide.

The process comprises two stages. The first stage is a direct reduction to form zinc from its oxides or salts, and volatilization of the zinc and of the lead oxide or salt contained in the starting material. The reduction takes place at the expense of the carbon contained in the carbonaceous material. The second stage is a vapour-phase oxidation of the zinc produced in the first stage, by the aid of a combustion supporter such as air and/or oxygen which is carried out concurrently with the zinc vapour formed.

The non-volatile content of the charge, which usually comprises CaO, SiO₂ and FeO, i.e. in an oxide state, and which contributes to form the slag, may have its concentrations of its various components so selected as to produce a slag at a melting point temperature not above 1200°C, so that non-volatiles may leave the reactor in the liquid phase. For this reason, it might be necessary to make appropriate additions to the starting materials if the concentrations of the components are not such as to fulfil the requirements specified hereinabove.

During the first stage, under determined and imposed conditions, metallic lead can be formed by the reaction:



The metallic lead mixes with the slag but separates therefrom by gravity.

The carbon monoxide which is collected about the rotation axis entrains the volatilized products upwards and is burned with oxygen so that additional heat can be supplied to the process.

The process is preferably carried out at a temperature of from 1100 to 1600°C.

Preferably, the process is carried out in a rotating frustoconical reactor such that solid phase adheres to the wall of the reactor and such that liquid phase flows out of the reactor through a drain hole in the bottom of the reactor. Thus, the process can be carried out in an apparatus as claimed in any claim of our patent application filed on the same day as the present application for an invention entitled "Apparatus For Recovering Metallic Materials".

One apparatus suitable for performing the process is characterised in that it is frustoconical

cal and is composed of one or more frustoconical trunks possibly replaced by their respective internal or external enveloping surfaces, the reactor comprising a metal casing internally lined by refractory materials and being rotated about its vertically arranged geometrical axis, a drain hole being formed through the reactor bottom wall so that the solid charged materials, due to the effect of the various phases, adhere to the inner reactor walls and the liquid substances which are formed are allowed to run down towards the drain hole, the inside diameter of the larger cone base being from 1 to 10 metres, the inside diameter of the lesser base being from 0.2 to 1 metre, the diameter of the drain hole being from 5 to 100% of the inside diameter of the cone lesser base, the angle of the generating lines of the cone with the vertical between from 10° to 60° , and the rotational speed of the reactor between from 10 to 80 revolutions per minute. Preferably, the generating lines of the conical surfaces do not have an inclination greater than 30° with respect to one another.

Reference will now be made, by way of example, to Figs. 1 and 2 of the accompanying drawing, showing reactors suitable for use in the invention.

The reactor is frustoconical, and consists of one or more conical frustums, possibly replaced by their external or internal enveloping surfaces. It is arranged so that its geometrical axis 1 is vertical. In use, the reactor is rotated about its axis 1. The reactor consists of a metal casing 2, internally lined with refractory bricks 3. The angular rotational speed and the angle 4 between the generating lines of the inner surfaces of the walls of the frustoconical bodies (or their enveloping surface) and the vertical is such that the solid phase of the material heated in the reactor remains, from a dynamic standpoint, in equilibrium under the concurrent actions of the weight, the inertial rotational forces, and the frictional forces on the inner wall, whereas the liquid phase runs down towards the reactor base, which has a drain hole 5.

The inside diameter of the larger base of the reactor is from 1 to 10 metres, preferably from 2 to 6 metres, whereas the inside diameter of the lesser base is from 0.2 to 1 metre.

The diameter of the drain hole is from 5% to 30% of the larger inside diameter, until reaching even 100% of the inside diameter of the lesser base depending upon the potential output of the installation.

The angle of the generating line of the cone to the vertical is from 10° to 60° , angles greater than 20° being preferred. In the case of a reactor consisting of more than one conical frustum or of an enveloped curved surface, the generating lines and their tangents preferably do not have a mutual inclination greater than 30° . In use, the rotational

speed of the reactor is usually from 10 to 80 rpm.

From two to four pipes or nozzles 6 and 7, with their ends opening into the inside of the inclined reactor, the nozzles being capable of being moved along a vertical axis, are used for charging both the feed material and the fuel. Alternatively, one or more pipes 8 (usually up to a maximum of four pipes) which are substantially parallel to the generating lines of the inner surface, may be used. Through perforations 9 formed along the entire pipe length and possibly evenly spaced apart from each other, preheated air and/or oxygen is continuously blown into the reactor. This jet of combustion aid has a radial centrifugal component and a tangential component relative to the path at the point where the jet impinges on the reactor wall and along a direction concordant with the motion so as not to disturb the dynamic conditions of the charge which is held in the reactor, either in the liquid phase or the solid phase.

Lastly, there is a central pipe 10 for introducing a combustion-aid, which is also used to burn the carbon monoxide formed and for bringing about oxidation of the zinc vapour.

The charge can be a primary raw material (an ore) and/or a secondary raw material (such as steelwork fumes, residual processing sludges and others) which contain lead and zinc in variable amounts such as from 1% and over. The particle size of the charge is usually from 0.01 to 5 mm.

The charge can be introduced in the upper section of the reactor after having been mixed with the fuel, the latter also being of fine particle size. Alternatively, the charge and fuel can be fed separately through the pipes 6 and 7 so as to obtain a sufficient head evolution consistently with the desired temperatures, and also in order to provide a reducing environment in the upper section.

In the lower section of the oven, through one of the pipes which is not otherwise used, the carbon-containing material is introduced to ensure the necessary thermal and processing (reducing) conditions.

The quantity of carbon used is a function of the quantity of zinc and is usually from 8% to 25% of the charge, preferably from 15% to 20% thereof.

As a combustion supporter, air, possibly preheated to 600°C and enriched with oxygen, or pure oxygen, possibly preheated to 200°C , are used.

The reaction velocity is very high by virtue of the considerably large contact surface area between the individual phases, this being a direct consequence both of the fine particle size of the charge and fuel and the rotary motion of the reactor. The consumptions predicted are nearly stoichiometric.

An Example will now be given to illustrate the invention.

EXAMPLE

The starting material is a steelwork fume containing 20% of zinc and 3.5% of lead.

- 5 The reactor is a frustoconical vessel flared downwards, and comprises a sheet metal casing internally lined with a refractory sleeve. The diameter of the larger base of the cone (upper section) was 3800 mm, the diameter of the base of the lesser cone (lower section) was 800 mm, the height of the frustum of cone was 3000 mm, and the angles of the generating lines of the cone with respect to the vertical were 45° and 10°, respectively,
- 10 for the upper and lower sections. The rotational speed of the cone was 20 rpm, the oxygen flow rate was 5 normal cubic metres per minute, the feed rate for the cone was 4 kg per minute, and the feed rate of the charge was 65 kg per minute. The charge was admixed with 0.10 kg of coke per kg of charge, the coke being intended as auxiliary coke.

- 15 Under these conditions, one obtains an oxide containing 60% of zinc and 10% of lead, with an output of 20 kg per minute and with yields of zinc and lead of the order of magnitude of 93%–95% and over.

CLAIMS

- 30 1. A process for treating a particulate material containing zinc in combined form, which comprises heating the material in the presence of a carbonaceous material so as to reduce the zinc in combined form to metallic zinc and so as to volatilize the metallic zinc, and effecting oxidation of the zinc in the vapour phase in the presence of air and/or oxygen.
- 35 2. A process according to claim 1, wherein the particulate material additionally contains lead in combined form, the lead in combined form being volatilized as such or as lead oxide, for being reduced to metallic lead.
- 40 3. A process according to claim 1 or 2, wherein the particulate material is heated to a temperature of from 1100 to 1600°C.
- 45 4. A process according to any of claims 1 to 3, wherein the particulate material has a particle size of from 0.01 to 5 mm.
- 50 5. A process according to any of claims 1 to 4, wherein the carbonaceous material is in particulate form.
- 55 6. A process according to claim 5, wherein the carbonaceous material has a particle size of from 0.01 to 5 mm.
- 60 7. A process according to any of claims 1 to 6, wherein the air and/or oxygen is pre-heated to a temperature of from 200 to 600°C.
- 65 8. A process for recovering or concentrating zinc and lead from primary or secondary raw material comprising admixing the material with coal, partial combustion of the carbon to produce CO, characterised in that it is carried out in two stages, in the first of which there is a direct reduction of the zinc by reaction with

- carbon contained in a carbonaceous compound and the volatilization of both the zinc and the lead oxide, the temperatures which are required being attained by partially burning with air and/or oxygen the carbon to CO, the material which contains zinc and lead being in the appropriate particle size, in the second stage a gaseous-phase oxidation takes place of the zinc as produced in the first stage, with the aid of air and/or oxygen.

9. A process according to any of claims 1 to 8, the process being carried out in a rotating frustoconical reactor such that solid phase adheres to the wall of the reactor and such that liquid phase flows out of the reactor through a drain hole in the bottom of the reactor.

10. A process according to claim 9, the process being carried out in an apparatus as claimed in any claim of our patent application filed on the same day as the present application for an invention entitled "Apparatus For Recovering Metallic Materials".

11. A process according to claim 1, substantially as hereinbefore described with reference to Fig. 1 or Figure of the drawing.

12. The product of a process according to any of claims 1 to 11.

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